SURFACE AND INTERFACIAL PROPERTIES

Plan of the subject:

- Surface tension,
- Interfacial tensions,
- Surface films
- Surface-active agents. (Surfactants)
- Application in EOR

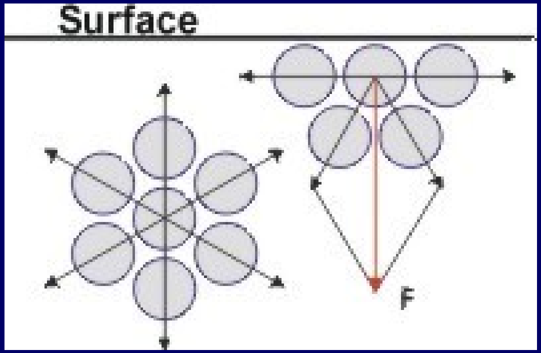
Types of interfaces

- *Interface* is the boundary between two or more phases
  exist together
- The properties of the molecules forming the interface are different from those in the bulk that these molecules are forming an *interfacial phase.*
- Several types of interface can exist depending on whether the two adjacent phases are in solid, liquid or gaseous state.
- Important of Interfacial phenomena in our daily life:
  - ✓ Adsorption of drugs onto solid adjuncts in dosage forms
  - ✓ Penetration of molecules through biological membranes
  - ✓ Emulsion formation and stability
  - ✓ The dispersion of insoluble particles in liquid media to form
    - suspensions.

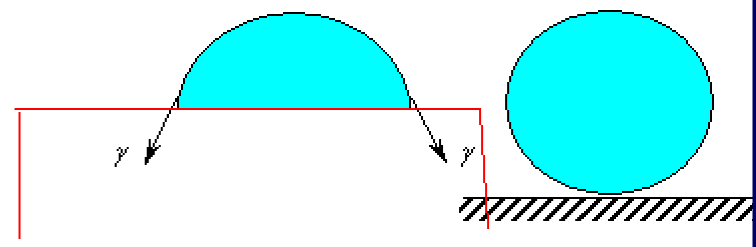
- **Soaps and detergents have been known to mankind for quite a long time.**
- A formula for soap consisting of water, alkali and cassia oil was written on a Babylonian clay tablet around 2200 BC.
- The Ebers papyrus (Egypt, 1550 BC) indicates that ancient Egyptians bathed regularly and combined animal and vegetable oils with alkaline salts to create a soap-like substance.
- A soap factory with bars of scented soap was found in the ruins of Pompeii (79 AD).
- Legend has it that soap gets its name from Mount Sapo where ancient Romans sacrificed animals. Rain would send a mix of animal tallow and wood ash down the mountain and into the clay soil on the banks of the Tiber. Eventually, women noticed that it was easier to clean clothes with this "soap".

(ii) Physical origin of surface tension

- A molecule at the surface, is missing half its attractive interactions, which is why when segregated to the surface, a liquid molecule is in an unfavorable energy state. This is the fundamental reason that ***liquid adjust their shape in order to expose the smallest possible surface area.***



- The interior molecules are equally attracted by all neighboring molecules with the same force, so that the resulting force is zero.

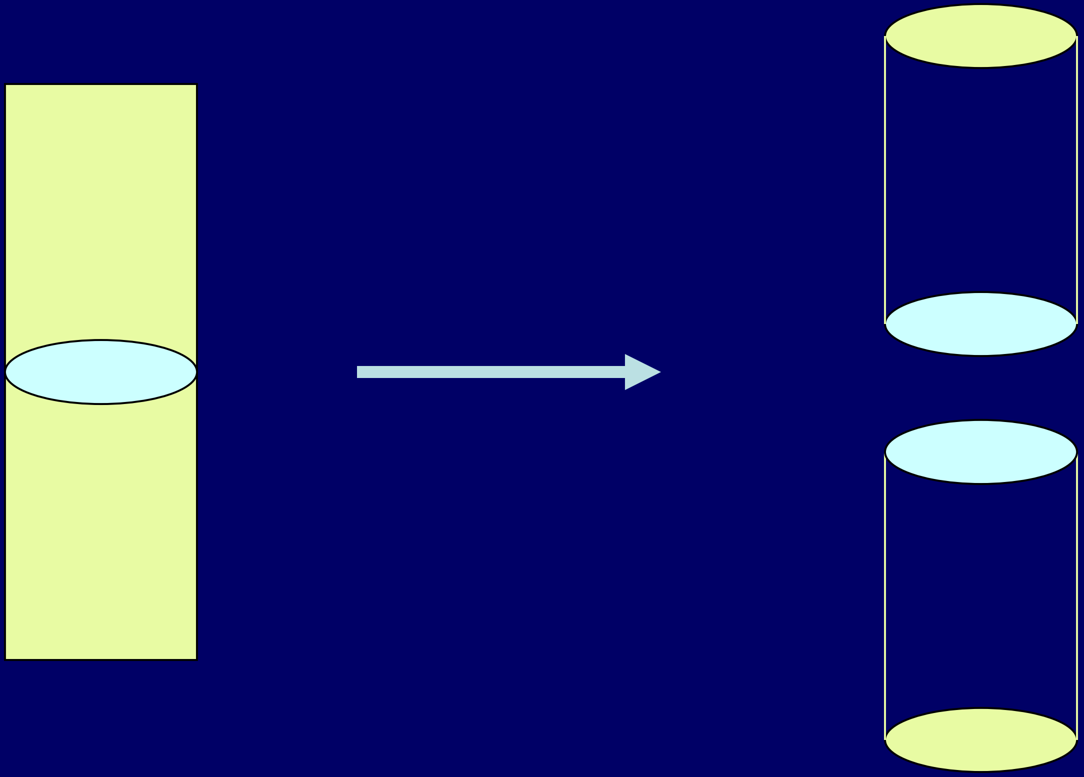


- The molecules at the surface are attracted by molecules from inside, whereas no force from outside the surface. Hence the resulting force is towards the interior of the liquid.

- The surface tension then causes drops of liquid to be round since the surface of the liquid is being minimized that way.

To keep the equilibrium, an equal force must be applied to
oppose the inward tension in the surface.

Formation of Surface



Separation of liquid requires work against cohesion forces

Formation of Surfaces? - *Unfavorable!*

- Therefore formation of surface is always accompanied by an increase in the free energy
  ($\Delta G_\Omega > 0$)
- Therefore formation of surface is always *unfavorable*

Surface Tension

- Surface tension (σ or γ) - increase in free energy as a result of formation of 1 unit (cm^2, m^2) of surface

$$\sigma = \left(\frac{\partial G}{\partial \Omega}\right)_{p,T} ; \quad \sigma > 0 \text{ (always positive!!)}$$

- Formation of surface of square $\Delta\,\Omega$ results in increase in the free energy ΔG:

$$\Delta G_{\Omega} = \sigma \cdot \Delta\Omega > 0$$

Another definition of surface tension

- Definition: γ s the magnitude *F* of the force exerted parallel to the surface of a liquid divided by the length *L* of the line over which the force acts.
- Units: N/m or dynes/cm

Thus SURFACE TENSION [γ] is the force per unit length that must be applied parallel to the surface so as to counterbalance the net inward pull and has the units of dyne/cm

INTERFACIAL TENSION is the force per unit length existing at the interface between two immiscible liquid phases and has the units of dyne/cm.

Measurement of surface tension

Methods for measuring surface and interfacial tension – three will be discussed:

1- Capillary rise method
2- Ring (Du Nouy) tensiometer
3- Drop weight method (Stalagmometer)

The choice of the method for measuring surface and interfacial tension depend on:

- Whether surface or interfacial tension is to be determined.
- The accuracy desired
- The size of sample.

The work W required to create a unit area of surface is known as *SURFACE FREE ENERGY/UNIT AREA* (ergs/cm^2)

erg = dyne . cm

$$\boxed{W = \gamma \Delta A}$$

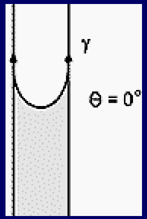
Its equivalent to the surface tension γ

Thus the greater the area A of interfacial

contact between the phases, the greater the free energy.

- If a capillary tube of inside radius =r immersed in a liquid that wet its surface, the liquid continues to rise in the tube due to the surface tension, until the upward movement is just balanced by the downward force of gravity due to the weight of the liquid
- *The upward component of the force* resulting from the surface tension of the liquid at any point on the circumference is given *by:*

$$\boxed{a = \gamma \cos \theta}$$

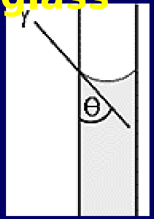


Cont. angle water and glass

Thus the total upward force around the inside circumference of the tube is

$$\boxed{a = 2 \pi r \gamma \cos \theta}$$

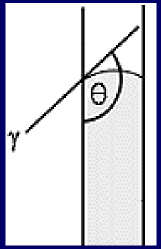
Where



θ = the contact angle between the surface of the liquid and the capillary wall

2 π r = the inside circumference of the capillary.

For water the angle θ is insignificant, i.e. the liquid wets the capillary wall so that cos θ = unity



Cont. angle Mercury and glass

The downward force of gravity

(mass x acceleration) is given by

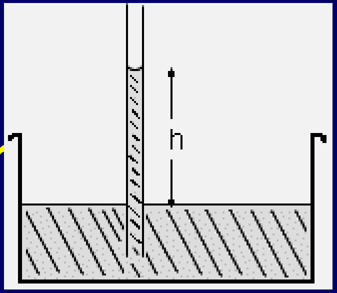
$$\pi r^2 h (p - p^o) g + w$$

Where:

πr^2 = **the cross sectional area**

h = **the height of the liquid column to the lowest point of the meniscus**

$(\rho - \rho o)$ = **the difference in the density of th liquid p and its vapor po**



g = **the acceleration of gravity**

w = **the weight of the upper part of the meniscus.**

At Maximu **h equilibrium**

$$2 \pi r \gamma \cos \theta = \pi r^2 h (p - p o) g + w$$

lly be disr

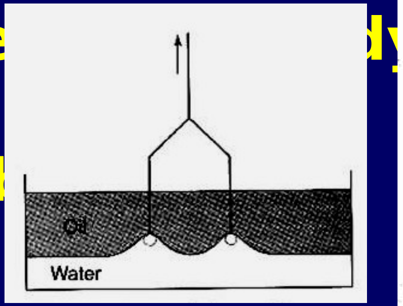
$$2 \pi r \gamma = \pi r^2 h p g$$

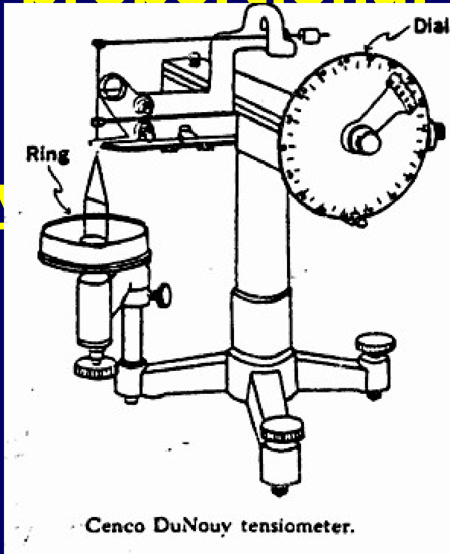
$$\gamma = 1/2 r h p g$$

Hence the surface tension can be calculated.

Ring (Du Nouy) Tensiometer

- **For measuring surface and interfacial tensions.**
- **The principle of the instrument depends on the fact that:**
  the force necessary to detach a platinum-iridium ring immersed at the surface or interface is proportional to the surface or interfacial tension.
- **The force of detachment is re dy on a calibrated dial**





Cenco DuNouy tensiometer.

- **T ven b**

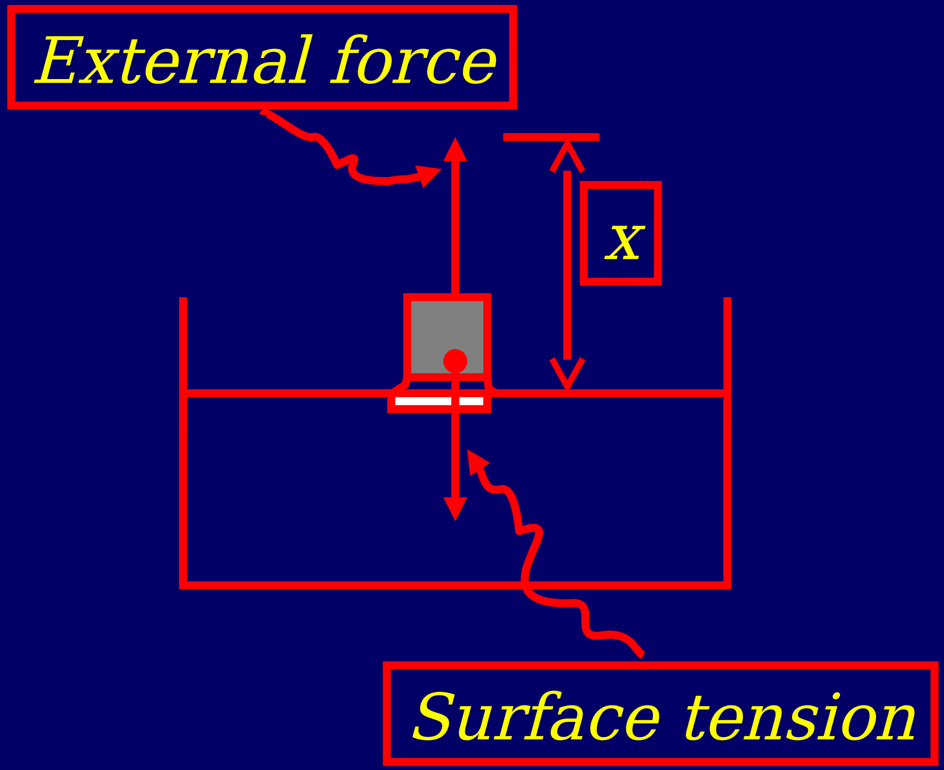
$$\gamma = F / 2 \pi (R_1 + R_2)$$

Where:

F = the detachment force

R_1 and R_2 = the inner and outer radii of the ring.

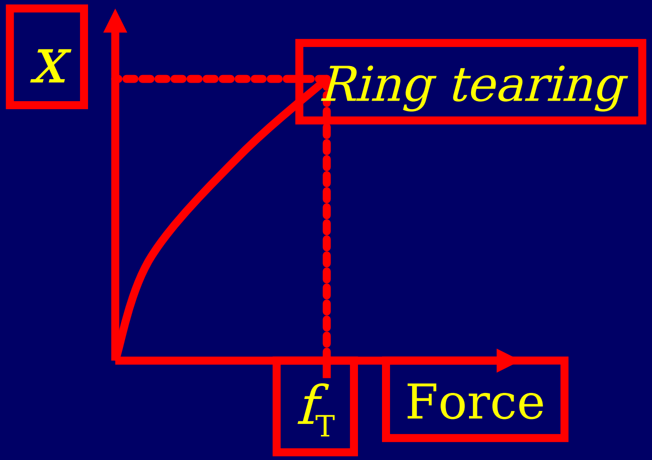
“Ring tearing” technique



External force

x

Surface tension



x

Ring tearing

f_T

Force

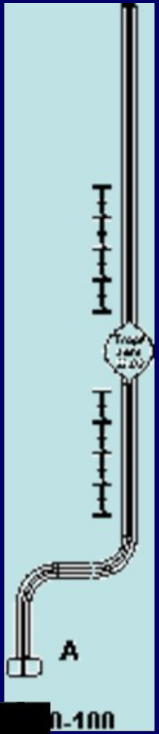
$$\sigma = \frac{f_T \cdot \beta(\text{correction factor})}{2 \cdot \{\text{ring circumference}\}}$$

Drop Weight and drop volume method

If the volume or weight of a drop as it is detached from a tip of known radius is determined, *the surface and interfacial tension* can be calculated from

$$\gamma = \frac{\Phi\, mg}{\pi r} = \frac{\Phi\, V pg}{2\, \pi\, r\, 2}$$

Where m = the mass of the drop
V = the volume of the drop
p = the density of the liquid
r = the radius of the tip
***g* = the acceleration due to gravity**
Φ = a correction factor

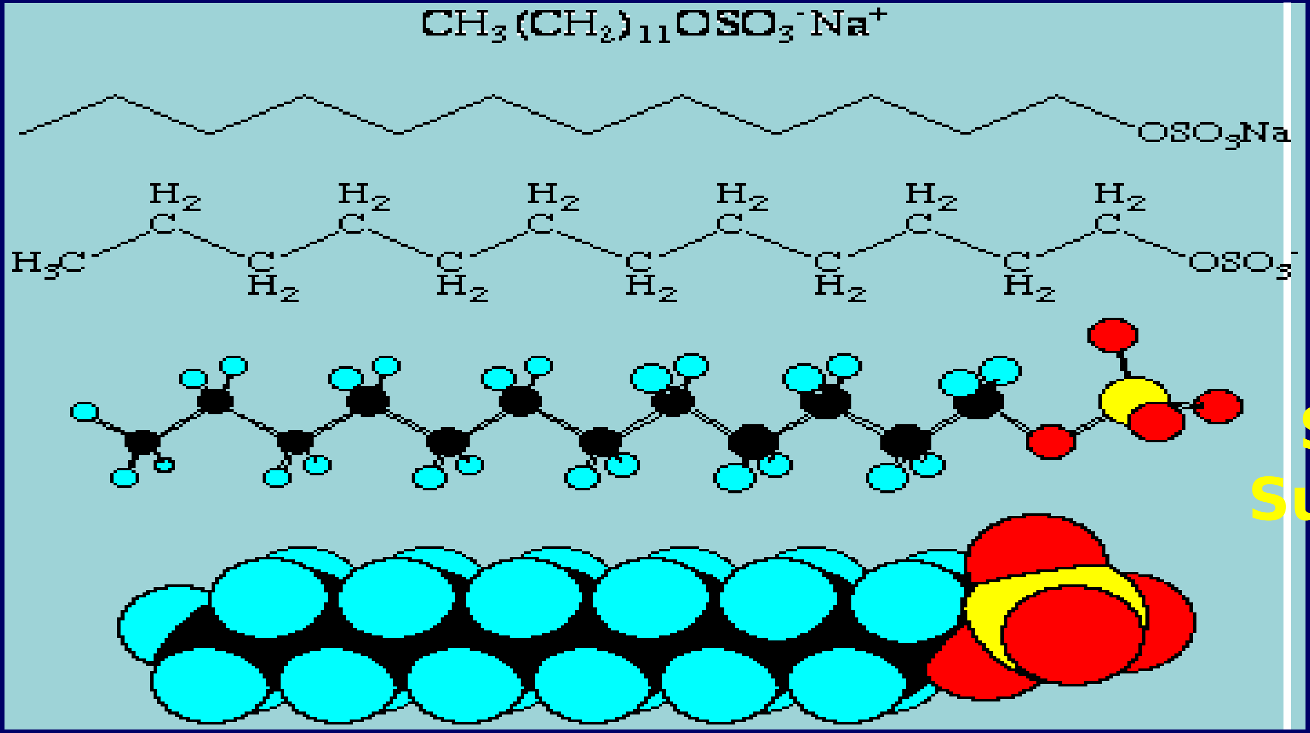


- ***The correction factor is required as n t all the drop leaves the tip on detachment***
- ***The tip must be wetted by the liquid so as the drop doesn't climb the outside of the tube.***

Surface Active Agents (SURFACTANTS)

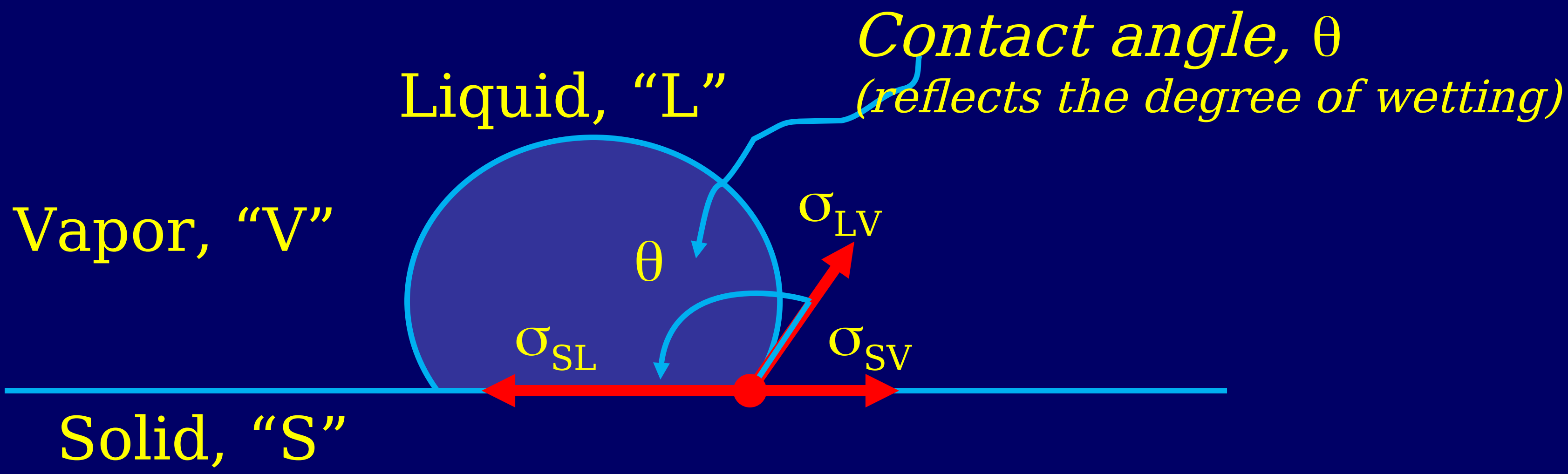
A surfactant molecule is depicted schematically as a cylinder representing the hydrocarbon (hydrophobic) portion with a sphere representing the polar (hydrophilic) group attached at one end.

The hydrocarbon chains are straight because rotation around carbon-carbon bonds bends, coils and twists them.



Sodium Lauryl Sulfate molecule

Drop on a Solid Surface



Contact angle, θ

(reflects the degree of wetting)

Liquid, “L”

Vapor, “V”

θ

σ_{LV}

σ_{SL}

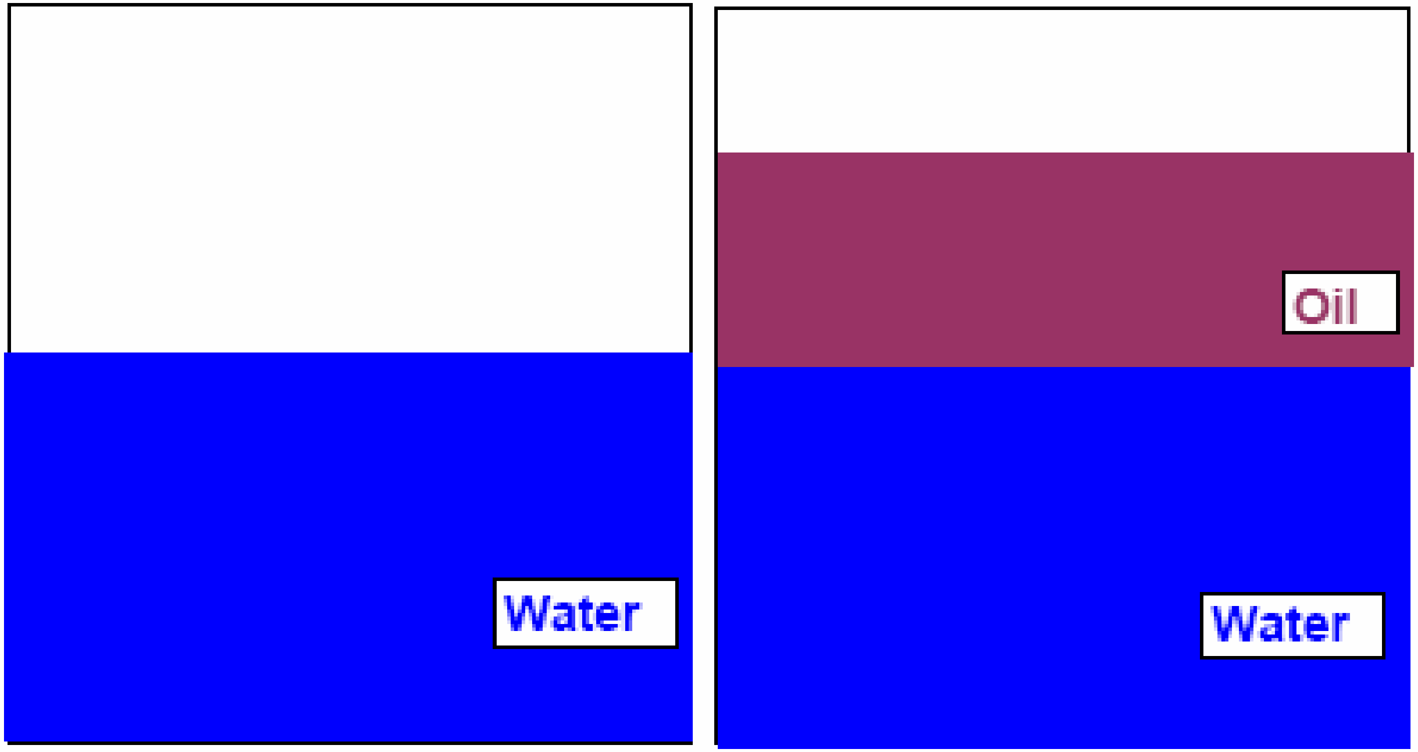
σ_{SV}

Solid, “S”

Young’s equation relates interfacial tensions and contact a

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cdot \cos\theta$$

How to reduce the surface tension of water?



- **Remove the Hydrogen Bonding Contribution**
  - Cover the Surface with Oil
  - 25 mN/m instead of 73mN/m

SURFACTANTS

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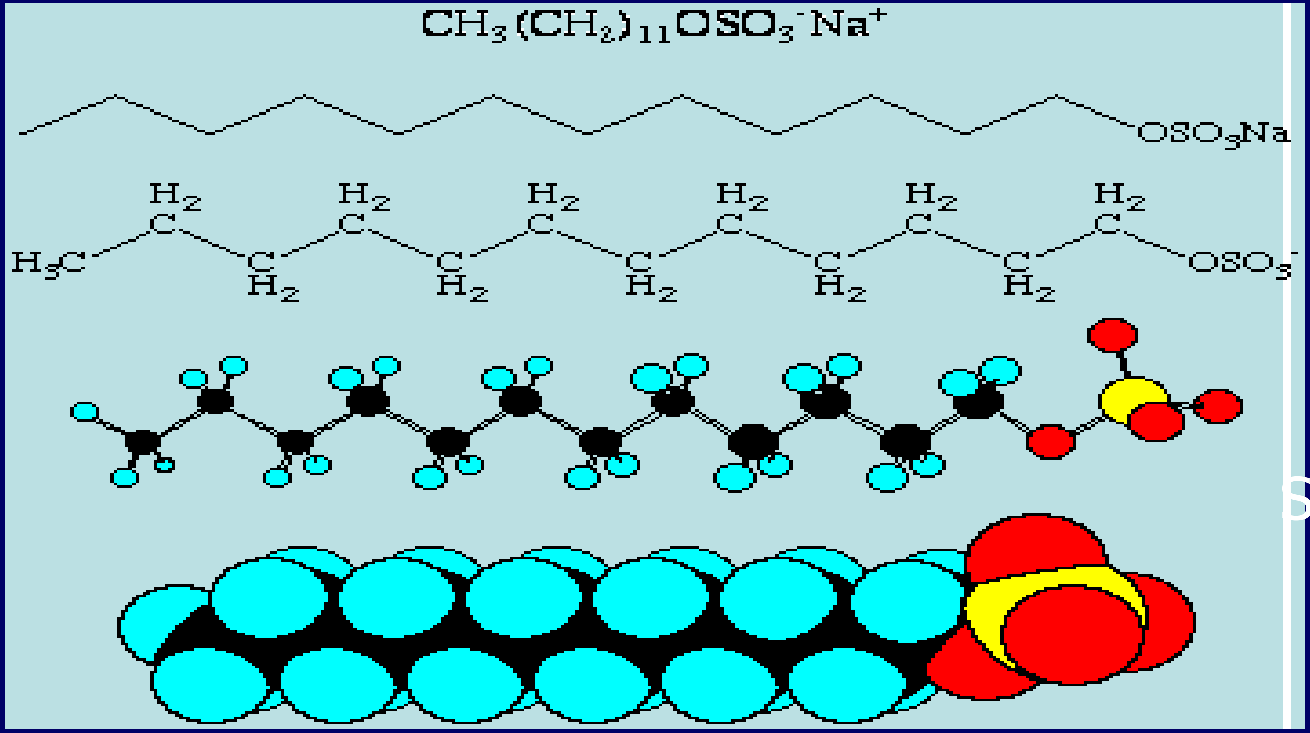


Sodium Lauryl Sulfate molecule

termed *surface active agents,* surf*actants.*

- The molecule or ion has a certain affinity for both polar and nonpolar solvents.
- Depending on the number and nature of the polar and nonpolar groups present, the amphiphile may be *hydrophilic, lipophilic* or be reasonably well-balanced between these two extremes.
- It is the amphiphilic nature of surface active agents which causes them to be adsorbed at interfaces, whether these be

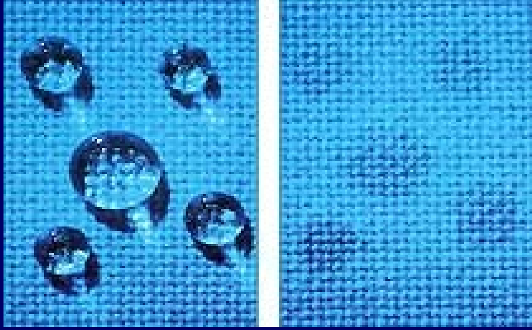
Classification of Surface Active Agents

Classification Based on Function

According to their use, surfactants can be divided into the following groups:

1. Wetting agents
2. Solubilizing agents
3. Emulsifying agents
4. Dispersing, Suspending and Deflocculating agents
5. Foaming and antifoaming agents
6. Detergents

Wetting agents-1



- Wetting agent is a surfactant that when dissolved in water, lower the contact angle and aids in displacing the air phase at the surface and replacing it with a liquid phase.
- Solids will not be wetted if their critical surface tension is exceeded than the surface tension of the liquid. Thus water with a value of 72 dynes/cm will not wet polyethylene with a critical surface tension of 3 1 dynes/cm.
- Based on this concept we should expect a good wetting agent to be one which reduces the surface tension of a liquid to a value below the solid critical surface tension.

According to the nature of the liquid and the solid, a drop of liquid placed on a solid surface will adhere to it or no. which is the wettability between liquids and solids.

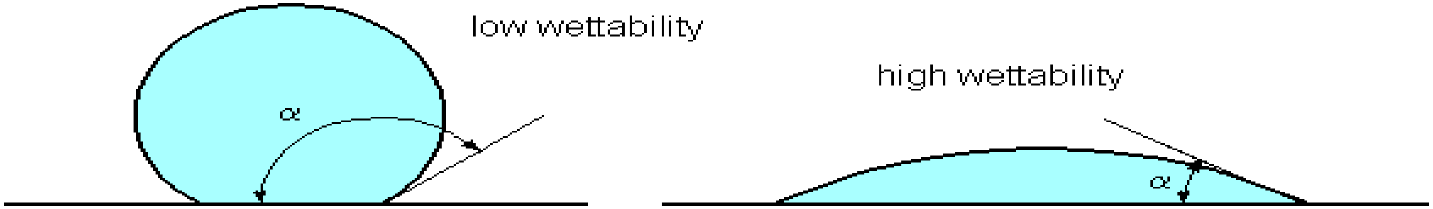
When the forces of adhesion are greater than the forces of cohesion, the liquid tends to wet the surface and vice versa.

If the contact angle is:

lower than 90°, the solid is called wettable

more than 90°, the solid is named non-wettable.

A contact angle equal to zero indicates complete wettability.

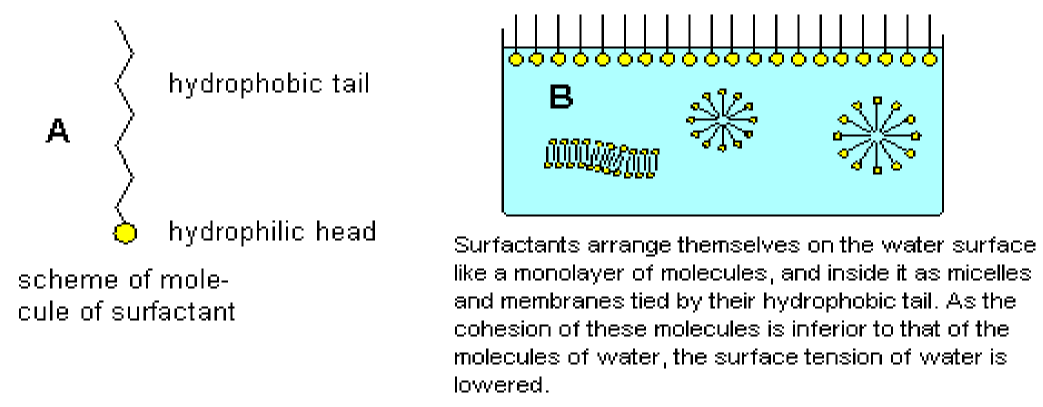


[redacted] The contact angle of a liquid with a solid is used as wettability index. For $\alpha < 90°$ the liquid wet the wall (eg: water on glass), for $\alpha > 90°$ the liquid does not wet the wall (eg: mercury on glass). If $\alpha = 0°$ the liquid perfectly wet the wall.

FORMATION OF MICELLES

As a Surface active substance contains a hydrophilic and a hydrophobic portions, it is adsorbed as a monolayer at the interfaces.

At water-air interface



scheme of molecule of surfactant

Surfactants arrange themselves on the water surface like a monolayer of molecules, and inside it as micelles and membranes tied by their hydrophobic tail. As the cohesion of these molecules is inferior to that of the molecules of water, the surface tension of water is lowered.

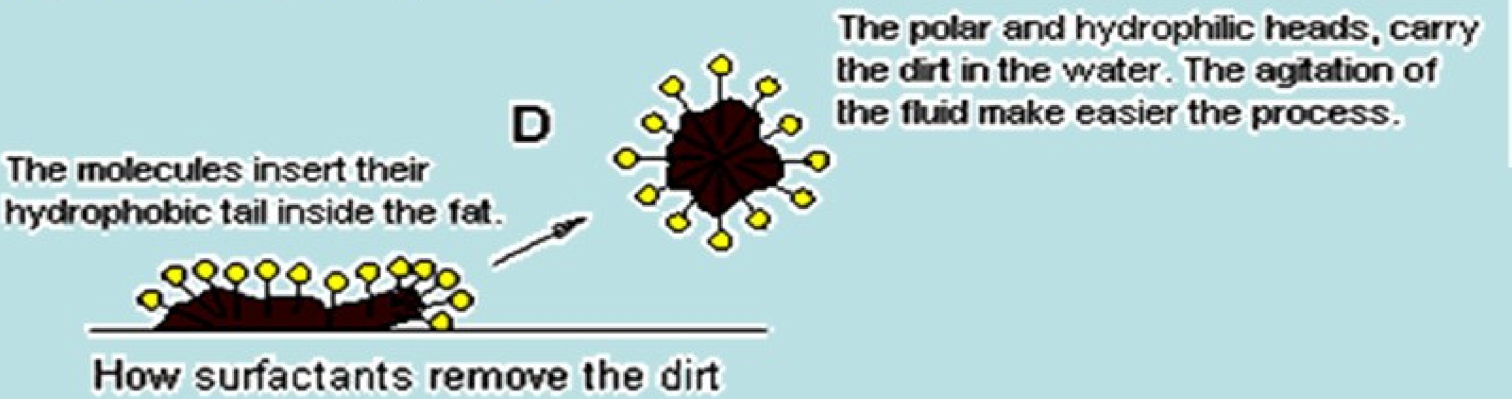
Surfaceactive molecules will be adsorbed at water-air interfaces and oriented so that the hydrocarbon chains are pushed out of the water and resu on the surface, while the polar groups are inside the water. Perhaps the polar groups pull the hydrocarbon chains partly into the water.

At oil-water interface

Surfaceactive molecules will be oriented so that the hydrophobic portion is inside the oil phase and the hydrophilic portion inside the water phase.

DETERGENTS

- Detergents are surfactants used for removal of dirt.
- Detergency involves:
  - Initial wetting of the dirt and the surface to be cleaned.
  - Deflocculation and suspension, emulsification or solubilisation of the dirt particles
  - Finally washing away the dirt.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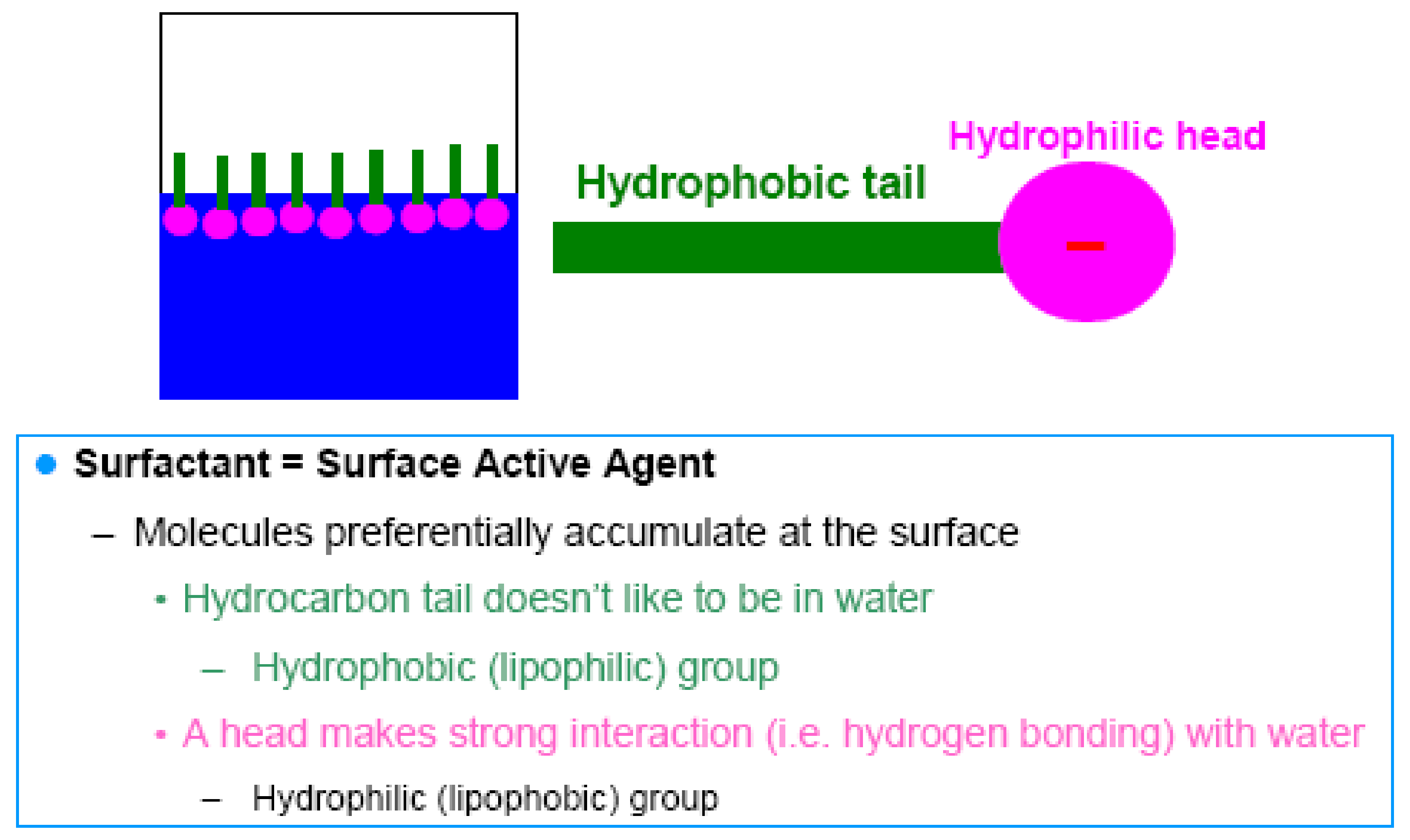
The polar and hydrophilic heads, carry the dirt in the water. The agitation of the fluid make easier the process.
The molecules insert their hydrophobic tail inside the fat.

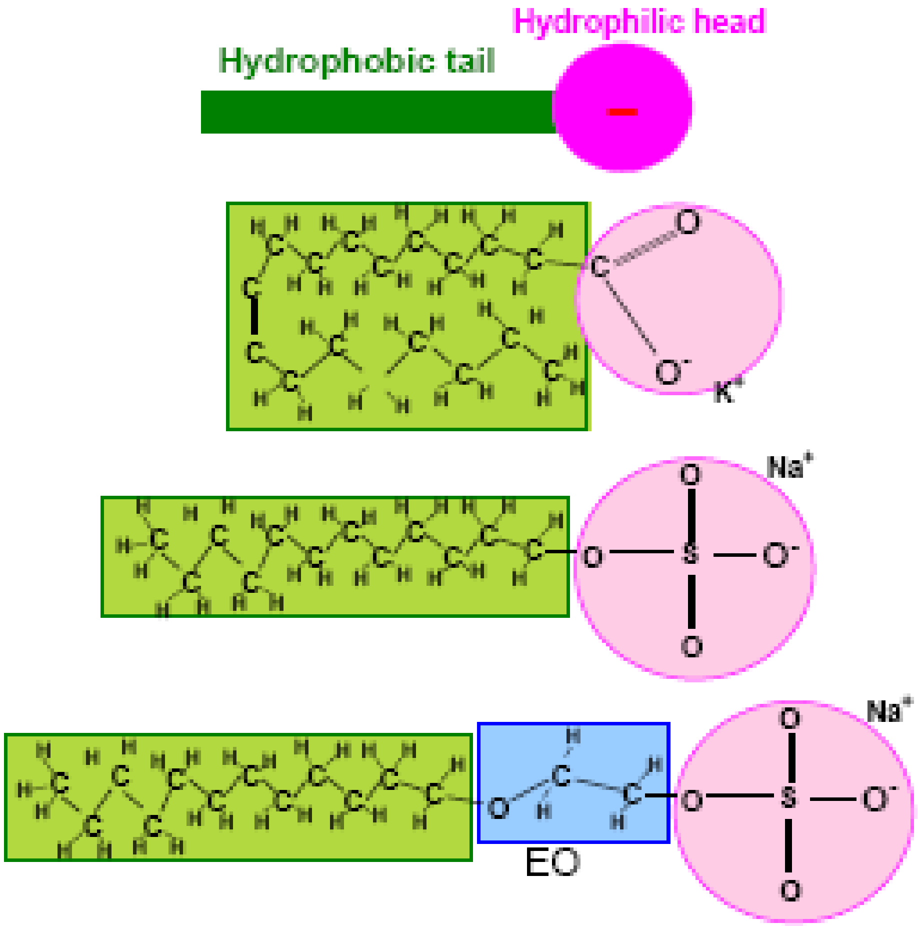
How surfactants remove the dirt

How to maintain stable oil layer on water?



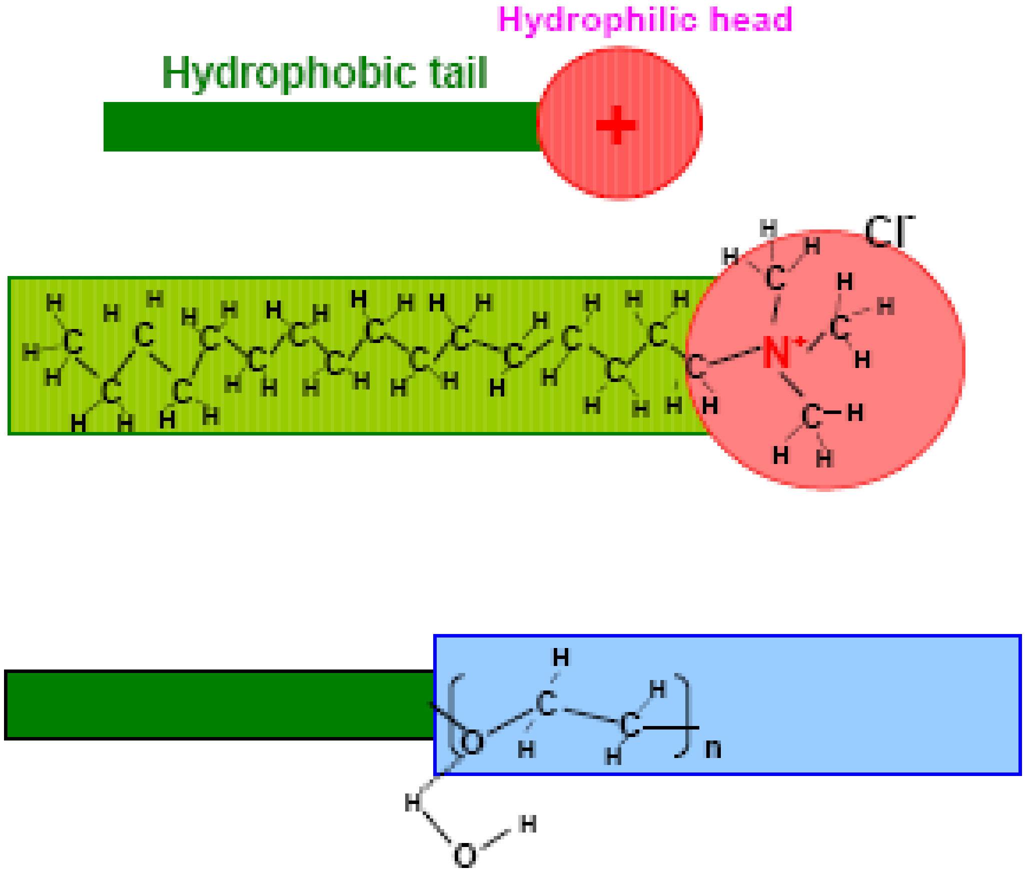
- **Surfactant = Surface Active Agent**
  - Molecules preferentially accumulate at the surface
    - Hydrocarbon tail doesn't like to be in water
      - Hydrophobic (lipophilic) group
    - A head makes strong interaction (i.e. hydrogen bonding) with water
      - Hydrophilic (lipophobic) group

Surfactant = Surface Active Agent



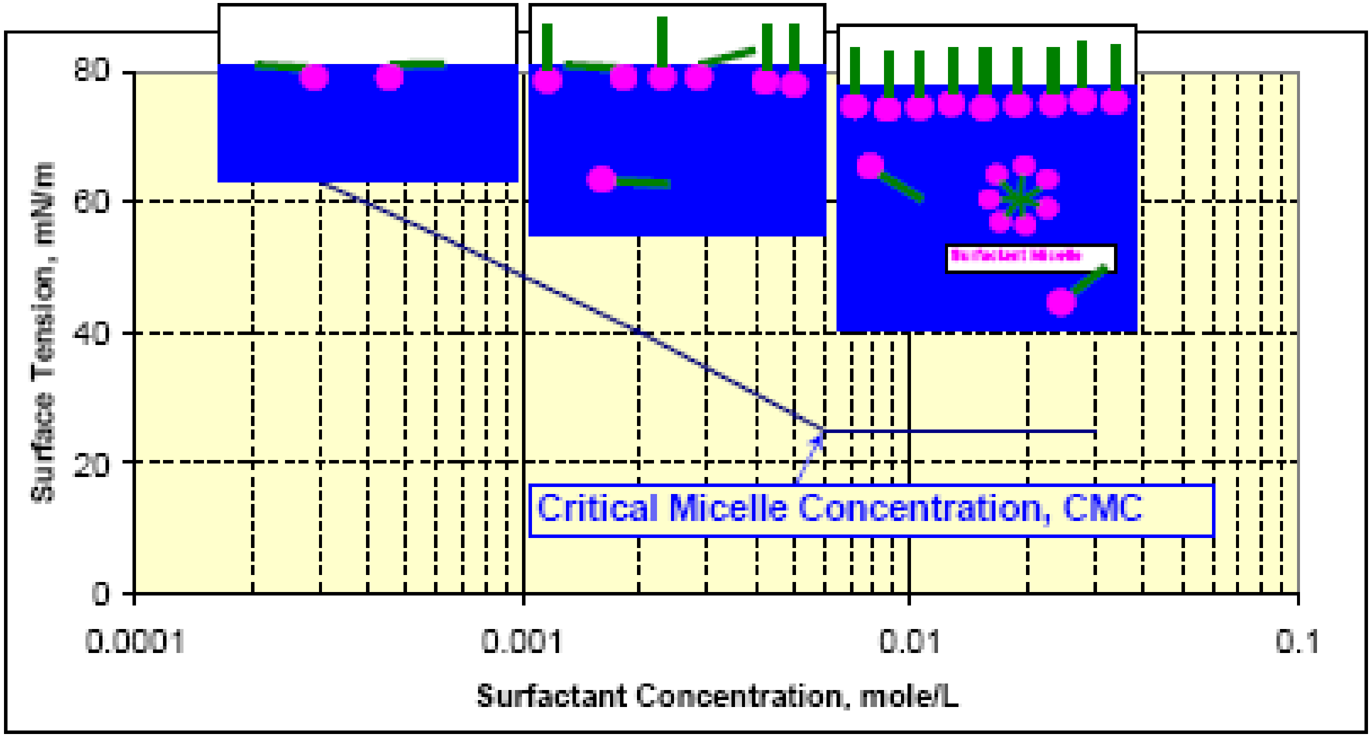
- Classified based on charge nature of the hydrophilic group
  - Anionic Surfactant
    - Soap: i.e. Potassium salt of fatty acid (K-Oleate)
    - Sodium salt of Dodecyl sulfonate (SDS)
    - with Ethylne Oxide group $(EO)_n$

Surfactant = Surface Active Agent



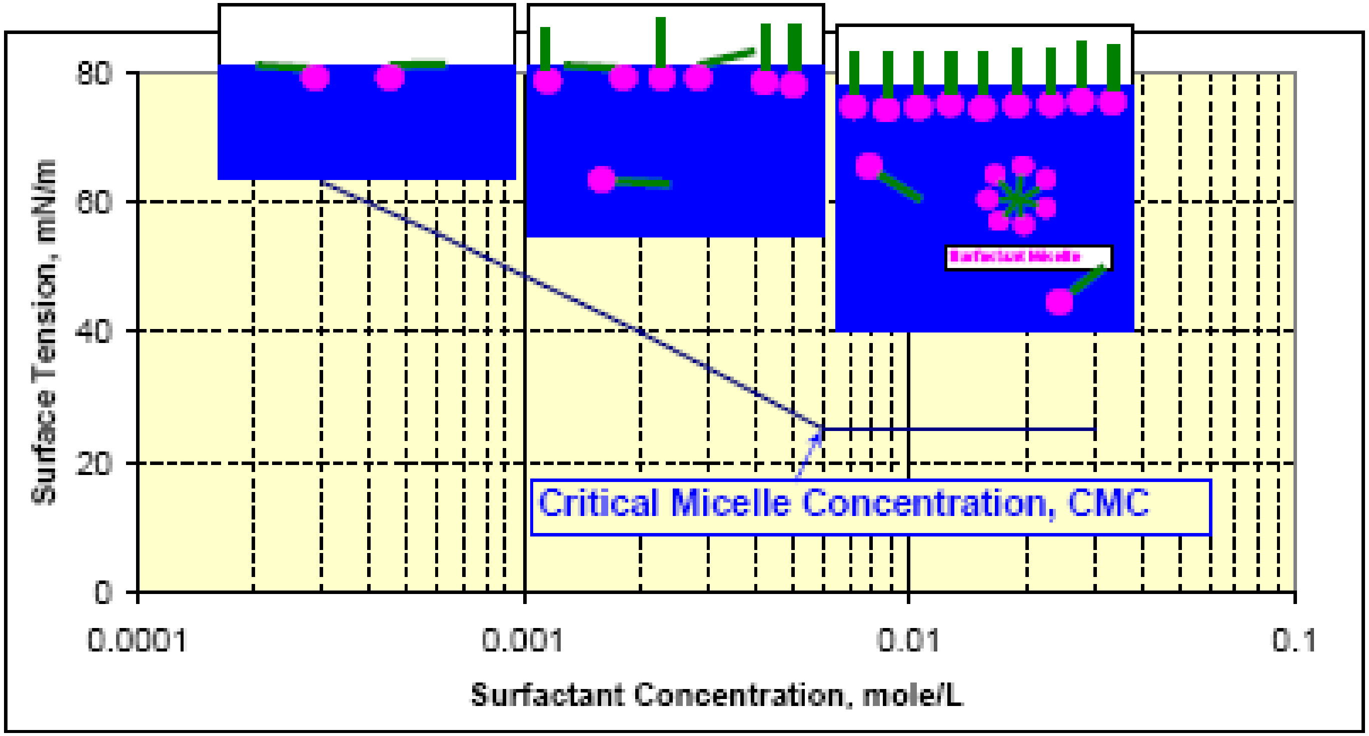
- **Cationic Surfactant**
  - Hydrocarbon chain with Amines
- **Non-ionic Surfactant**
  - Ethylene Oxide chains
  - Could be a large molecule (10<n<50)

Micelle Formation



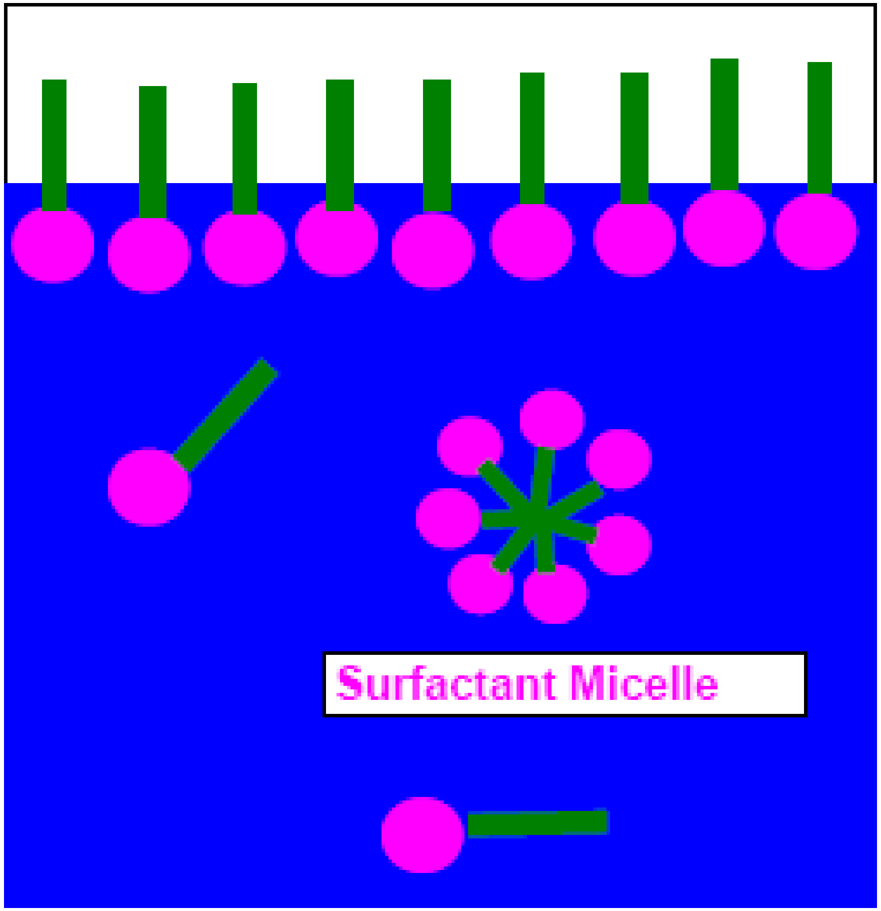
- Surface tension drops as surfactant molecules accumulate at the surface
- Once the surface is fully covered, the surfactant molecules aggregate and form micelles in water
  - Hydrophilic groups toward water and hydrocarbon chains in the mice

Micelle Formation



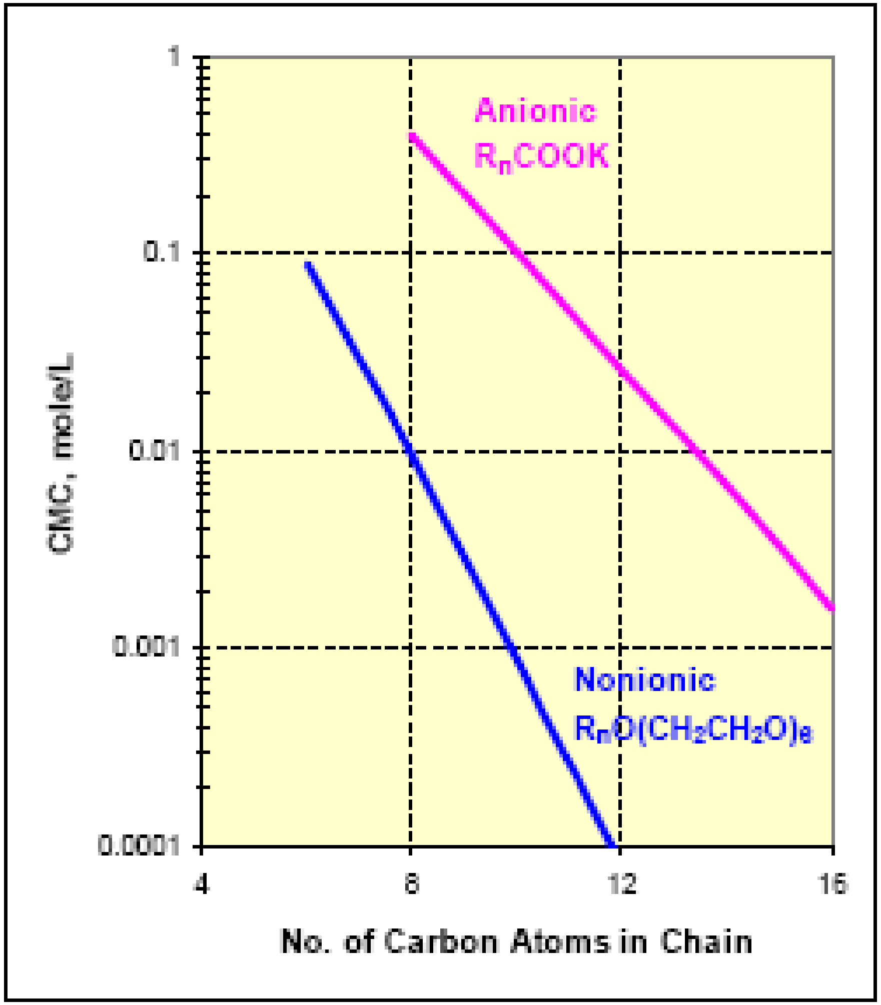
- Minimum surfactant concentration for micelle formation: Critical Micelle Concentration, CMC
  - Surface tension remains constant at above CMC
  - No. of Micelles increase at higher concentration

Critical Micelle Concentration



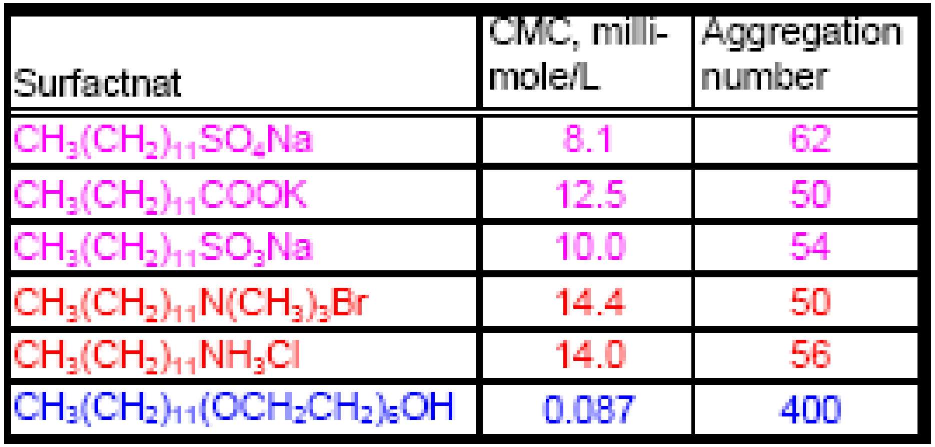
- Higher the surfactant concentration, more micelles
- Micelle size does not change
- Oil will dissolve into micelles and forms swollen micelles

Critical Micelle Concentration

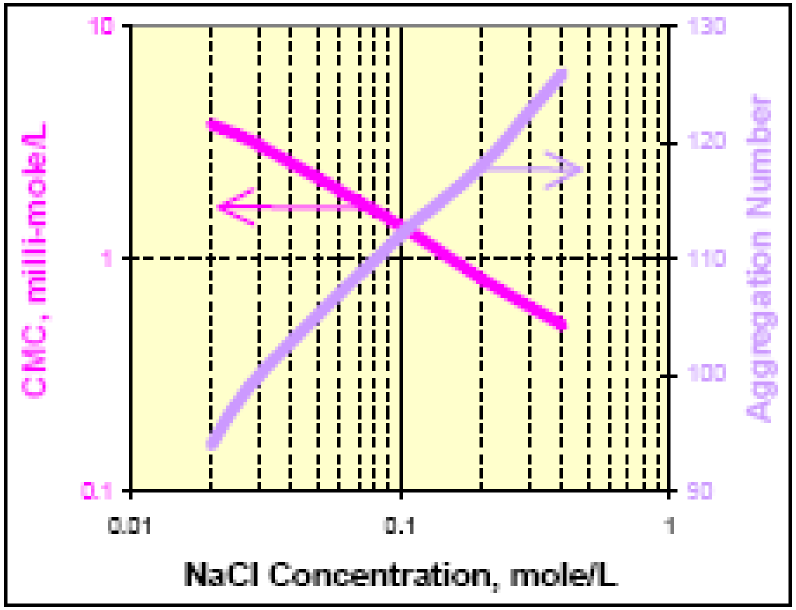


- Lower CMC with longer hydrocarbon chain surfactant
- **Lower CMC and bigger size micelles with Non-ionic Surfactants**
  - No Coulombic repulsion between hydrophilic groups
  - Length of $(Ch_2CH_2O)_n$ has little effect on CMC, but increase micelle size with larger n

Critical Micelle Concentration



Surfactnat	CMC, milli-mole/L	Aggregation number
$CH_3(CH_2)_{11}SO_4Na$	8.1	62
$CH_3(CH_2)_{11}COOK$	12.5	50
$CH_3(CH_2)_{11}SO_3Na$	10.0	54
$CH_3(CH_2)_{11}N(CH_3)_3Br$	14.4	50
$CH_3(CH_2)_{11}NH_3Cl$	14.0	56
$CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$	0.087	400



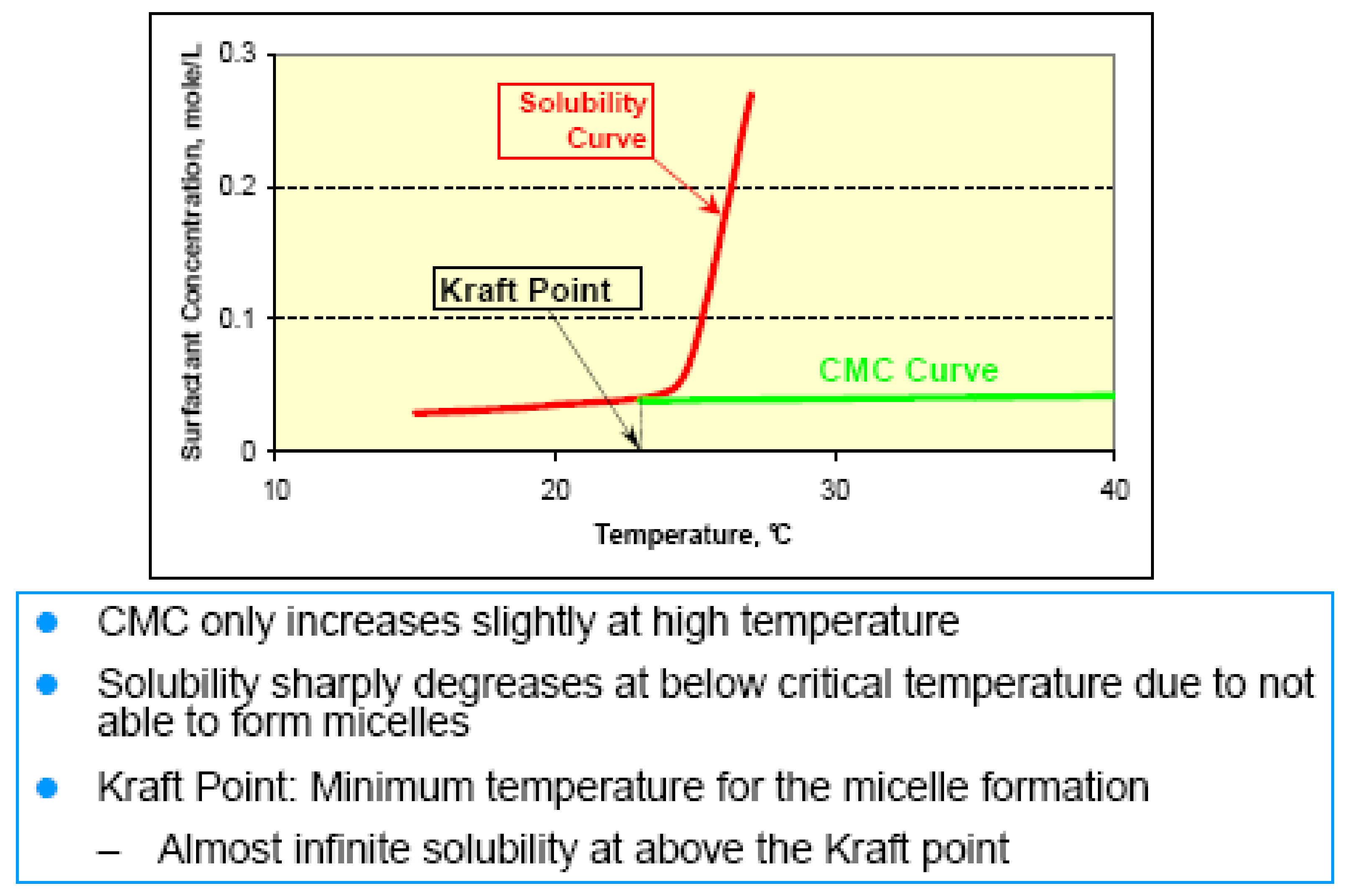
Ionic Surfactants:

- 50-60 surfactant molecules / micelle
- Addition of electrolytes reduces the number of CMC but provide large micelles

Non-ionic surfactants

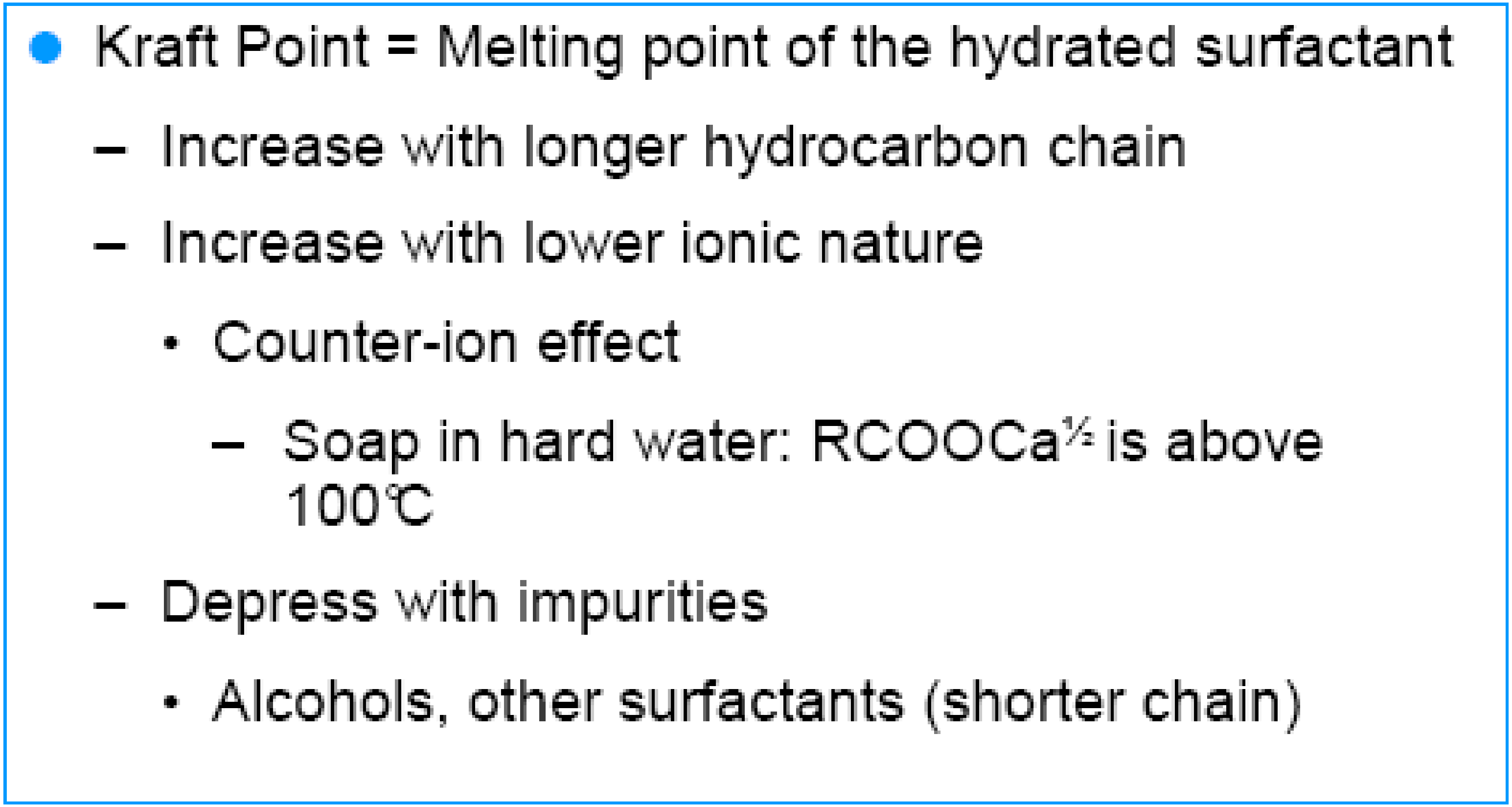
- Lower CMC and bigger micelles

IONIC SURFACTANTS



- CMC only increases slightly at high temperature
- Solubility sharply degreases at below critical temperature due to not able to form micelles
- Kraft Point: Minimum temperature for the micelle formation
  - Almost infinite solubility at above the Kraft point

Kraft Point



- Kraft Point = Melting point of the hydrated surfactant
  - Increase with longer hydrocarbon chain
  - Increase with lower ionic nature
    - Counter-ion effect
      - Soap in hard water: $\mathrm{RCOOCa}^{1/2}$ is above 100℃
  - Depress with impurities
    - Alcohols, other surfactants (shorter chain)

Reservoir Rock-Fluid Interaction

Reservoir fluid flow is governed by complex interactions between the fluids and the reservoir rock. These interactions become more complicated when, as is often the case, *two or more* fluids are present in the same pore. When a driving force acts on such systems, the fluids compete in motion, because their movement is mutually dependent. To appropriately describe the simultaneous flow of two or more fluids in a porous medium requires a good understanding of both the fluid-fluid and rock-fluid interactions.

Reservoir Rock-Fluid Interaction